

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY


(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 04 SEP 2006

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Applicant's or agent's file reference 1468WO		FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/BE2005/000045		International filing date (day/month/year) 01.04.2005	Priority date (day/month/year) 02.04.2004	
International Patent Classification (IPC) or national classification and IPC INV. C03B19/06 C03C14/00 C04B35/01 F27D3/02				
Applicant VESUVIUS CRUCIBLE COMPANY				
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 3 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>				
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>				
Date of submission of the demand 14.09.2005		Date of completion of this report 29.08.2006		
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized officer Burtan, M-M Telephone No. +31 70 340-8972		



**INTERNATIONAL PRELIMINARY REPORT
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International application No.
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Box No. I Basis of the report

1. With regard to the **language**, this report is based on
- ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3(a) and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4(a))
 - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1, 3-5	as originally filed
2, 2b	received on 01.12.2005 with letter of 30.11.2005

Claims, Numbers

1-7	received on 01.12.2005 with letter of 30.11.2005
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- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-7
	No: Claims	-
Inventive step (IS)	Yes: Claims	1-7
	No: Claims	-
Industrial applicability (IA)	Yes: Claims	1-7
	No: Claims	-

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

1. Reference is made to the following document:

D1: US-A-3 429 486 (COPE GERALD R ET AL) 25 February 1969 (1969-02-25)

2. The document D1 discloses (the references in parentheses applying to this document):

a refractory stopper-head used in handling of molten steel, made from tar-impregnated fused silica, consisting essentially of silica and bentonite bound with a chemical binder; a process for manufacturing said stopper-head, comprising the steps of: molding the fused silica and bentonite with 4% water, casting the batch into plaster molds, firing the cast stopper heads at about 980 °C (1800 °F), impregnating the stopper-heads with liquid tar (or pitch) at about 200 °C (400 °F) and baking the impregnated stopper-heads to cokify the tar (column 2, lines 39-67).

3. The subject-matter of independent claims 1 and 6 differs from this known refractory stopper head in that the shape of the article renders it suitable for conveying or guiding solidified material. The subject-matter of independent claims 1 and 6 is therefore new (Article 33(2) PCT).

4. The problem to be solved by the present invention may be regarded as reducing the tin pick-up and the resulting damage on the surface of the solidified material. The solution to this problem proposed in claims 1 and 6 of the present application is considered as involving an inventive step (Article 33(3) PCT) for the following reasons: there is no disclosure and no hint in the available prior art that the material of the proposed stopper head (a vitreous silica basis impregnated with a carbonaceous material) could be used to manufacture articles for conveying or guiding solidified material. The skilled person, when faced with the proposed problem, would not be able to arrive at the solution proposed in the present application without the exercise of inventive step.

5. Claims 2 - 5 and 7 are dependent on claims 1 and 6, respectively, and as such also meet the requirements of the PCT with respect to novelty and inventive step.

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6. The invention of the present application being susceptible of industrial application, the requirements of Article 33(4) PCT are also being fulfilled.

the end of a molten tin bath and the beginning of an annealing line. Shaped carbon blocks are provided under the scrapper rollers to scrap the surface of the rollers and remove any tin carried by the glass ribbon and released at the surface of the roller. As a matter of fact, it has been observed that the scrapper blocks force some tin into the porosity of the roller. After years of service, a substantial proportion of the tin is oxidized. The resulting tin oxide damages the roller surface and marks the glass ribbon.

[0008] In another known application (described for example in USP 4,412,503) refractory segments of vitreous silica are used to guide a steel wire in a galvanisation bath. After some time, an important pickup of mixed tin and iron oxides can be observed at the surface of the segment, in contact with the wire, resulting in a serious marking of the wire.

[0009] Several attempts have been made in that art to try to improve the properties of vitreous silica with respect to pickup. So far, the most common approach has been to use a material other than vitreous silica for particularly demanding applications (such as high silicon steel for example). It has thus already been suggested to provide the rollers with special alloy coatings (USP 2,695,248), or to use a shaft made from a particular steel grade (USP 4,470,802).

[0010] It has also been proposed to use a roller made from a different material such as graphite or having a layer made from a material with a lamellar structure such as talc, graphite or boron nitride (FR-A1-2672586).

[0011] Some good results have been obtained with relatively "soft" graphite rollers or graphite coated rollers which do not tend to accumulate pickup at their surface. With such articles, it has been observed that the outer layer of the articles on which the pickup is formed tends to be eroded by the sheets, strips or foils carried by the articles faster than the deposit formation so that no pickup can be observed. An obvious disadvantage of such articles being that due to their weak erosion resistance, they must also often be replaced with all the above discussed problems.

[0012] It is therefore an object of the present invention to provide refractory articles for guiding or conveying a solidified material which possess the excellent mechanical properties of vitreous silica articles without showing the pickup problems normally observed with the articles of the art. Such articles should also have a prolonged service life.

[0013] These problems and others have been solved with articles for guiding or conveying a solidified material comprising a vitreous silica basis and, homogeneously distributed therein a carbonaceous material.

[0014] According to a first embodiment, the vitreous silica basis is comprised of a chemically bonded (cement bonded and/or resin bonded) vitreous silica aggregate. Typically, the chemically bonded vitreous silica aggregate is prepared from a mixture comprising (i) at least 75 wt. %, preferably more than 85 wt. %, of amorphous silica, (ii) from 2 to 23 % of a chemical binder and (iii) water. Suitable chemical binders are calcium aluminate, calcium silicate, polyalkoxysiloxanes such as polydiethoxysiloxane (ethylsilicate), colloidal silica, aluminium or zirconium acetate, magnesium oxide, and the like or mixtures thereof. Calcium aluminate is the

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preferred binder. The mixture is shaped and then dried. It is generally not necessary to fire such a chemically bonded vitreous silica aggregate. The dried chemically bonded vitreous silica

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Claims.

1. Refractory article for guiding or conveying a solidified material comprising a vitreous silica basis impregnated with a carbonaceous material.
- 5 2. Refractory article according to claim 1, wherein the article comprises 1 to 6 wt. % of carbonaceous material.
3. Article according to claim 1 or 2, wherein the refractory article consists of a chemically bonded vitreous silica comprising from 75 to 96 wt. % of vitreous silica, from 2 to 23 wt. % of a chemically binder and from 2 to 4 wt. % of water.
- 10 4. Article according to claim 3, wherein the chemical binder is selected among the group consisting in calcium aluminate, calcium silicate, polyalkoxysiloxanes, colloidal silica, zirconium acetate, magnesium acetate, magnesium oxide and their mixtures and preferably is calcium aluminate.
- 15 5. Article according to claim 1 or 2, wherein the refractory article is sintered and comprises at least 60 wt. %, preferably more than 90 wt. %, more preferably more than 95 wt. % and even more preferably more than 99 wt. % of amorphous silica.
- 20 6. Process for the preparation of a refractory article according to any one of claims 1 to 6, characterized in that it comprises the step of
b) impregnating a vitreous silica basis with a carbonaceous material, preferably under heat and/or pressure.
7. Process according to claim 6, characterized in that the impregnation step is followed by a further step of
c) cracking the impregnated carbonaceous material under heat, preferably under pressure.